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(56) Documents Cited

**GB 1374832 A      GB 1362991 A      GB 0781803 A  
EP 0026666 A1      WO 99/64638 A      WO 98/49371 A1  
US 4187155 A      US 4157285 A**

(58) Field of Search

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7/02 , C25F 1/12 1/14 1/16 1/18  
Online: WPI, EPODOC, JAPIO**

(54) Abstract Title

**Electrolytic reduction of sintered mass of metal oxide**

(57) A method of electrolytic reduction of a metal oxide, in particular titanium dioxide, wherein said electrolysis is preformed on a sintered mass of a mixture of metal oxide substantially comprising particles of size greater than 20 microns and finer particles of less than 7 microns. The sintered mass is preferably formed by mixing binder and water. The finer particles may make up 5 - 70% by weight of the mass.

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### Improved Feedstock for Electrolytic Reduction of Metal Oxide.

PCT Patent Application WO99/64638 describes a method of removal of oxygen from metal oxides and solid solutions by electrolysis in a fused salt, and has particular application to titanium dioxide reduction.

The possibility of producing inexpensive Ti and Ti alloy powders is of tremendous economic importance. Several attempts have been made using the process described above with varying degrees of success. A problem with this process is that to get reduction of the oxide electrical contact must be maintained for some time at a temperature at which oxygen diffuses readily. Under these conditions the titanium will diffusion bond to itself resulting in clumps of material stuck together rather than free flowing powder.

It is an object of the invention to overcome this problem by providing a feedstock for the process which overcomes these problems.

The invention comprises a method of electrolytic reduction of a metal oxide wherein said electrolysis is preformed on a sintered mass of a mixture of metal oxide substantially comprising particles of size generally greater than 20 microns and finer particles of less than 7 microns.

Preferably the finer particles make up between 10 and 55% of the sintered block by weight.

High density granules of approximately the size required for the powder are manufactured and then are mixed with very fine unsintered titanium dioxide, binder and water in the appropriate ratios and formed into the required shape of feedstock. This feedstock is then sintered at to achieve the required strength for the reduction process. The resulting feedstock after sintering but before reduction consists of high density granules in a low density (porous) matrix.

The feedstock can be reduced as blocks using the usual method and the result is a friable block which can easily be broken up into powder. The reason for this is that the matrix shrinks considerably during the reduction resulting in a sponge-like structure, but the granules shrink to

form a more or less solid structure. The matrix can conduct electricity to the granules but is easily broken after reduction.

#### Example

About 1 kg of rutile sand (titanium dioxide content 95%) from Richard Bay Minerals, South Africa, with an average particle size of 100  $\mu\text{m}$  was mixed with 10 wt.% rutile calciner discharge from the company TiOxide (made from the sulphate process) which had been ground in a pestle and mortar to ensure a fine particle agglomerate size. To this was added a further 2 wt.% binder (methyl cellulose) and the whole mix was shaken with a mechanical shaker for 30 minutes to ensure a homogenous feedstock. The resulting material was then mixed with distilled water until the consistency of the paste was about that of putty. This material was then flattened by hand onto a sheet of aluminium foil to a thickness of about 5 mm and then scored, using a scalpel blade, into squares of side 30 mm. This material was then allowed to dry overnight in a drying oven at 70°C. On removal from the oven it was then possible to peel off the foil and break the rutile into squares as marked by the scalpel blade. The binder gives significant strength to the feedstock thus enabling a 5 mm diameter hole to be drilled in the centre of each square for mounting on the electrode at a later stage. Since no shrinkage was anticipated in the sintering stage no allowance for shrinkage in the calculation of the hole size was necessary.

About 50 squares of the rutile were loaded up into a furnace in air at room temperature and the furnace was switched on and allowed to heat at its natural rate to 1300°C (time to heat up around 30 minutes). After 2 hours at this temperature the furnace was switched off and allowed to cool at its natural rate (about 20°C per minute initially). When the rutile was below 100°C it was unloaded from the furnace and stacked onto a M5 threaded stainless steel rod which was to be used as the current carrier. The total amount of rutile loaded was 387 g. The bulk density of the feedstock in this form was measured and found to be  $2.33 \pm 0.07 \text{ kg/l}$  (i.e. 55% dense), and its strength for handling was found to be quite sufficient.

The feedstock was then electrolysed using the process described in the above referenced patent application at up to 3V for 51 hours at an electrolyte temperature of 1000°C. The resulting material after cleaning and removal of the electrode rod had a weight of 214 g. Oxygen and

nitrogen analysis indicated that the levels of these interstitials were 800 ppm and 5 ppm respectively. The form of the product was very similar to that of the feedstock except the colour change and slight shrinkage. Due to the process used to manufacture the feedstock the product was friable and could be crushed up using fingers and pliers to a reasonably fine powder. Some of the particles were large therefore the material was passed through a 250  $\mu\text{m}$  sieve. Approximately 65% by weight of the material was small enough to pass through the 250  $\mu\text{m}$  sieve after using this simple crushing technique.

The resulting powder was washed in hot water to remove the salt and very fine particles, then it was washed in glacial acetic acid to remove the CaO and then finally in water again to remove the acid. The powder was then dried in a drying oven overnight at 70 °C.

The results can be expressed as the concentration of calciner discharge required to achieve useable strength of the feedstock after sintering. At 1300°C about 10% was required, at 1200°C about 25% was required and at 1000°C at least 50% was required although this still gave a very weak feedstock.

The calciner discharge used can be replaced by cheaper amorphous  $\text{TiO}_2$ . The key requirement for this 'matrix' material is that it sinters easily with significant shrinkage during the sintering process. Any oxide or mixture of oxides which fulfil these criteria would be usable. For  $\text{TiO}_2$  this means the particle size must be less than about 1  $\mu\text{m}$ . It is estimated that at least 5% matrix material should be present in order to give any significant strength to the sintered product.

The starting granules need not be rutile sand but could be manufactured by a sintering and crushing process, and in principle there is no reason to suppose that alloy powders could not be made by this route. Other metal powders could also presumably be made by this route.

## Claims

1. A method of electrolytic reduction of a metal oxide wherein said electrolysis is preformed on a sintered mass of a mixture of metal oxide substantially comprising particles of size greater than 20 microns and finer particles of less than 7 microns.
2. A method of electrolytic reduction of metal oxide as claimed in claim 1 wherein said sintered mass is additionally formed by mixing binder and water.
3. A method as claimed in any preceding claim wherein said metal oxide is titanium oxide.
4. A method as claimed in any preceding claim wherein said finer particles make up between 5 and 70% of the sintered block by weight.
5. A method as claimed in any preceding claim wherein said finer particles make up between 10 and 55% of the sintered block by weight.
6. A feedstock for the electrolytic reduction of metal oxide, said feedstock comprising a sintered mass of a mixture of metal oxide particles of size greater than 20 microns and finer particles of less than 7 microns.
7. A feedstock as claimed in claim 6 wherein said metal oxide is titanium oxide.
8. A feedstock as claimed in claim 7 wherein said finer particles make up between 5 and 70% of the sintered block by weight.
9. A feedstock as claimed in claim 8 wherein said finer particles make up between 10 and 55% of the sintered block by weight.



Application No: GB 0010873.8  
Claims searched: 1-9

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Examiner: Pete Beddoe  
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## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.R): C1A APF6; C7B (BDCF, BDCJ, BDCK, BDCN, BDDA, BDDDB, BDDC, BEDG, BEDL)

Int Cl (Ed.7): C01G 23/047; C04B (35/043, 35/46, 35/482); C25C (3/00, 3/04, 3/06, 3/26, 3/28, 3/34, 5/00, 5/02, 5/04, 7/02); C25F (1/12, 1/14, 1/16, 1/18)

Other: Online; WPI, EPODOC, JAPIO

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 1374832 (MAGNESIUM) see esp ex 1 and p2 lines 61-85	6-9
X	GB 1362991 (UKAEA) see esp p1 lines 49-77	6-9
X	GB 0781803 (HORIZONS) see esp exs	1 at least
X	EP 0026666 A1 (SUMITOMO) see esp p2 lines 6-17 & ex 1	6-9
A	WO 99/64638 A1 (CAMBRIDGE UNIVERSITY) see whole doc	1
A	WO 98/49371 A1 (ALTA GROUP) see whole doc	1
X	US 4187155 (DIAMOND) see esp ex 1	1-5
A	US 4157285 (WINAND) see whole doc	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.